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(54) A method for safe transmission of steady or time-dependent pressure under high-low, steady or time-dependent temperature

(57) The present invention deals with the application and transmission of steady or time varying pressure under high/low, steady or time dependent temperatures and eliminates the potential danger for explosive events which is unavoidable in coventional techniques (with fluid media). The method consists of using an assembly of ceramic microspheres coated by a solid lubricant (for temperatures between -50°C and 1600°C and steady or monotonically increasing pressure) or a mixture of melted oxides with extremely high boiling points (for temperatures between 300° and 2700°C and steady or cyclically varied pressure). The invention is related to the fields or Mechanics of Materials, Fluid Mechanics, Technology of Ceramics, etc. The method is exemplified in the case of internal pressurization of tubular metallic specimens. The tests show uniform pressure transmission to the desired directions, very good efficiency (ratio of radial to axially imposed pressure), repeatability and elimination of the explosion danger and the associated costs.

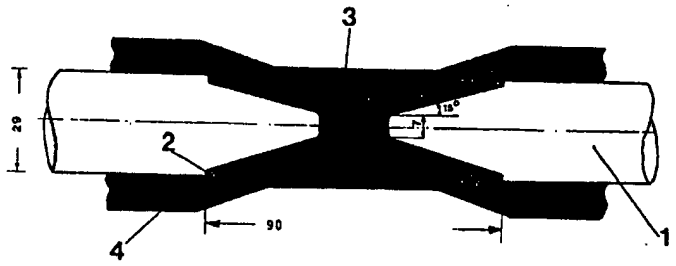

Figure 3

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Description

The present invention refers to a method for the safe application and transmission of steady and monotonically or cyclically varying pressure. It is based, depending on theconditions, on the use of a molten oxides mixture or an assembly of ceramic microspheres coated by solid lubricant. The method is operative for a wide range of temperatures, from very low (-50° C) to very high ones (up to 2700°C).

The major scientific and technical fields related directly with the invention include Mechanics of Materials, Fluid Mechanics, Technology of Glasses and Ceramics and industrial production processes where the simultaneous application of high pressure and temperature is required.

The current state-of-the-art uses fluid media for pressure transmission (liquids with low boiling point such as water, oils, etc. or gases for high temperature applications). A series of drawbacks, especially when high temperature prevails, are generally reported in these cases :

- Danger of explosive events due to rupture of specimen material with damaging and costly consequences for the overall installation.
- High capital and operational costs due to the required safety design and measures and the use of expensive and complicated facilities, particularly at high pressures.
- Limited available range of operating temperatures, especially when a usual liquid medium is employed (upper limit set by its boiling point).
- Inability to observe closely or to execute measurements with optical and other costly devices due to the potential danger for explosive events.

Recently, the use of a bed of mixed ceramic and graphite particles for shape casting of metallic materials has been reported (US patent 4, 667, 497). Some of the above drawbacks are then eliminated. On the other hand though, this method suffers from difficulties in transmitting pressure uniformly, the need to impose high axial loads in order to achieve adequate radial pressure values, and mainly, the inability to apply time varying pressure (fatigue tests) due to the non-linear behaviour of the bed during unloading (reduction of pressure). Evidently, any method that may substitute (at least partially) the commonly employed one (use of a fluid medium) should be competitive to the latter with reference to its basic advantages, namely the simplicity in geometric design and the uniformity of the transmitted pressure in all directions.

The present invention deals with a method for safe pressure transmission based on the use of different media depending on the prevailing temperature and the requirements of the application for constant or time varying pressure (mechanical fatigue) under constant or time varying temperature (thermal fatigue). More specifically :

- In the temperature range from -50°C to 1600°C, use is made of an assembly of ceramic microspheres of sizes between 5 and 500 μm, covered by a solid lubricant. This allows for the transmission of steady or monotonically increasing pressure under temperatures that may vary with time.
- For temperatures between 300°C and 2700°C, a mixture of melted oxides with a specified composition is employed, assuring suitable viscosities in the desired temperature range and offering the capability for the transmission of steady or time varying pressure under temperatures that may change with time in the above mentioned range.

For an efficient application of the method, the media used should satisfy the following requirements :

- The material of the microspheres should withstand high temperatures and pressures for long periods of time (hundreds of hours) and permit the production of uniformly sized spherical particles with reasonable costs. A systematic search led to the selection of the following ceramics : Al_2O_3 (alumina), SiO_2 (silica), silicon carbide, silicon nitride, ZrO_2 (partially or fully stabilised zirconia) and their mixtures. In addition, substantial improvements in the efficiency of the method and the reduction of the required axial load are realised by coating the microspheres with a high temperature resistant, solid lubricant such as boron nitride or molybdenum bisulfide.
- The mixture of melted oxides should be characterised by suitable glass transition temperature and low reactivity (basicity) when in contact with the pressurised metallic materials for long time periods (hundreds of hours) under the high pressures and temperatures of operation. Sufficient quantities of these oxides should be produced at an acceptable cost. Experimental work and literature search led to the basic composition of the oxides mixture shown below :

$$xB_2O_3 \cdot (1-x)\ SiO_2\ (O \leq x \leq 1)$$

where x is the mole fraction of B_2O_3.

According to the specific needs, this basic composition can be modified by adding appropriately small amounts of other oxides from the classes of glass formers, conditional formers and modifiers (see Table below). Small amounts of alkali and alkaline earth halide salts, sulfate or sulfide salts can be also added, depending on the desired range of temperatures.

i) Formers : GeO_2, Al_2O_3, P_2O_5, V_2O_5 As_2O_5, Sb_2O_5, Sb_2O_3, Ca_2O_3, ZrO_2, As_2O_3.

ii) Conditional Formers : TiO_2, MoO_3, WO_3, Cr_2O_3, ZnO, PbO, FeO, Fe_2O_3, CdO, ThO_2, In_2O_3, Bi_2O_3, PbO_2, SnO_2, HgO, MnO, CoO, NiO, BeO, SnO, TeO_2, Nb_2O_5, Ta_2O_5, HfO_2, ReO_2, TeO_2, RuO_2, OsO_2, Rh_2O_3, Ir_2O_3, IrO_2, PdO, PtO_2.

iii) Modifiers : Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, Sc_2O_3, Tl_2O, Tl_2O_3, CuO, Cu_2O, Ag_2O, Au_2O_3, R_2O_3 (R = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dh, Ho, Er, Tm, Hb, Lu), SeO_2, PaO_2, UO_3.

In relation to the aforementioned drawbacks of the techniques that use conventional fluid media, the present method exhibits significant improvements concerning :

- The elimination of the danger for explosive events at high pressures and temperatures.
- The considerable reduction in the costs of equipment, installation, etc.
- The capability to perform measurements and close observations with important consequences on the study of material behaviour.
- The extension of the available temperature range.
- The capability to perform safely fatigue tests (variable pressure and temperature) based on the proper selection of the transmitting medium for each case.

With regard to the principal advantage of the conventional techniques (with fluid media), i.e. the uniformity of the transmitted pressure in all directions, this is assured in the present method by :

a) the selection of suitable ceramic particle size distribution such that the system exhibits adequate "(pseudo) - fluidity". The latter is related to the ability of the particles to roll and slide against each other changing continuously the microscopic geometry of the pressure transmitting medium. The addition of high temperature resistant lubricants contributes to the enhancement of this property (pseudo-fluidity). Tests carried out with microspheres without lubricant coating do not result in satisfactory performance of the method due to relatively large frictional effects. Moreover, the use of the lubricating agent prevents atomic diffusion at the contact area between particles thus avoiding sintering phenomena that might otherwise occur under the high pressure and temperature conditions. It was found that boron nitride offers sufficient lubrication as its structure permits intracrystalline sliding (fig. 1).

b) the selection of the viscosity of the melted oxides mixture at the temperature range of interest, such that the minimum required fluidity of the medium is attained.

In the following paragraphs, a specific application of the invention is described with reference to the attached figures exemplifying the realisation of the method in the case of internal pressurization tests on a tubular specimen under elevated temperature. Two distinct possibilities are examined :

(i) Thermal fatigue and steady or monotonically increasing pressure

If thermal fatigue (from e.g. room to high temperatures) is required with the application of constant or monotonically increasing internal pressure, an assembly of spherical, stabilised zirconia particles is employed for pressure transmission. This material can sustain very high pressures before crushing and temperatures (up to 1800° C) without melting or sintering problems. The particles are prepared by means of the electrofusion process which permits the production of small (< 50 μm) spheres with the following composition :

ZrO_2 67%
SiO_2 30%
Others 3% (mainly Al_2O_3)

The microstructure is based on monoclinic zirconia crystals (microhardness : 9 GPa) uniformly embedded in silica glass (microhardness : 7 GPa). It is a result of the manufacturing process and specifically of the cooling and crystallisation method following the fusion of the mixture of oxides at high temperatures. The physical properties thus obtained are :

True relative density :	3.85
Bulk density :	2.3
Microhardness :	7-9 GPa

A testing programme has been undertaken to ensure the stable behaviour of the particles at conditions reaching 400 bar and 750°C for several hours. No sintering was observed macroscopically while the microscopic examination found no evidence of microcracking or any surface damage that could alter the shape of the beads. The role of silica glass in the required mechanical properties, the behaviour after thermal cycling, and the performance in repeated cycles of loading / unloading, were also the subject of intensive study using Scanning Electron Microscopy (SEM) with Energy Dispersed X-Ray Analysis (EDXA)

for Post-Experiment Examination of both the particles and the metallic structure. The preservation of the spherical particle shape is an important factor for the performance of the system as a pressure transmitting medium.

The procedure of covering uniformly the quite small and spherical zirconia particles (average diameter of 40 microns) with the lubricant is similar to the preparation of pharmaceutical tablets and involves ultrasonic cleaning of small batches of the spheres, coating by boron nitride in a slowly rotating glass container that is externally heated by air streams and internally periodically sprayed with water, and microwave drying of the batch to avoid the formation of agglomerations. The thickness of the lubricant layer on the individual particles is of the order of 1-10 μm, as shown by microscopy measurements.

A system of two specially designed contoured cylinders placed inside the test specimen cavity are called upon to compress the zirconia particles and introduce an internal pressure which gives rise to transverse stresses on the thin walled test specimen (Fig. 2).

The basic criteria for the efficiency of the method in comparison to the conventional fluid media include the uniformity of the developing radial pressure along the specimen gauge length and the ratio of radial to axial (vertical) pressure.

Detailed experimental data from the specimen with suitably configured compression pistons (fig. 3) show that the present system offers adequate pressure transmission efficiency (radial/axial pressure is equal to 0.51) and quite good uniformity along the specimen (deviations of the strain gauges from the central reference one are less than 0.13%, fig. 4). The relationship between the applied axial load and the obtained radial pressure on the specimen is linear during the loading phase, shows satisfactory repeatability during loading / unloading cycles (Fig. 5) and the unloading path is easily mathematically modelled. It was also shown that large plastic deformations of the specimen do not influence significantly the uniformity of the applied pressure or the ratio of radial to axial load.

(ii) Mechanical fatigue and time varying temperature

In cases requiring mechanical fatigue (cyclic variation of load) under temperatures higher than 500°C, the selected pressure trasmitting medium is a molten mixture of SiO_2 and B_2O_3. The temperature of operation ranges between 500° and 900°C with a B_2O_3 mole fraction of x=77.65 mol%. The dependence of viscosity n on temperature is described (for this specific composition) from the empirical relationship given below :

$$\log n = 3\,341 - 5145\,(1/T) + 5.79 \cdot 10^{6}\,(1/T)^{2}$$

where T is the temperature in K and the above relation applies in the range 400-1100°C. In fig. 6 the above equation is represented graphically (viscosity versus temperature). Similar expressions hold for different mixture compositions. The main factor determining the nature and the proportions of the oxides in the mixture is the attainment of viscosity values (in melted state) of the order of 10^4-10^6 Poise in the desired temperature range (definitely above the glass transition temperature of the mixture).

In the present application, this is accomplished in principle by varying the fraction of B_2O_3 (fig. 7) up to its extremes (with x=0, i.e pure SiO_2, very high operation temperatures of the method can be achieved, as the viscosity values of fig. 8 indicate). Furthermore, the addition of other oxides (as Li_2O in fig. 9, and GeO_2, Na_2O in fig. 10) contributes to the "adjustment" of viscosity in the temperature range of interest.

Concerning the reactivity issue, a series of tests took place in which fused B_2O_3 (at temperature 950°C) was left in contact with Ni alloys for time periods ranging from 4 to 40 hours. The Raman spectra of pure B_2O_3 and samples from the molten B_2O_3 after several hours of contact with Ni-alloy, have been compared showing that the spectrum remains practically unchanged. This leads to the conclusion that no reaction takes place between fused boron oxide, SiO_2 and Ni-alloy at least to a spectroscopically detectable scale. The tests were repeated with several alloys with the same results. The experimental data from internal pressurization of the tubular specimen with suitably configured compression pistons, indicate that the present system exhibits a ratio of radial to axial pressure almost equal to unity and excellent uniformity along the specimen gauge length. It is important to note that the relationship between the applied axial (vertical) load and the attained radial pressure remains linear during both the loading and unloading phases.

Finally, fluid mechanic calculations for the flow of a viscous liquid though slits have been performed to assess the potential danger of molten glass being ejected under high pressure from cracks during specimen rupture. For slits with dimensions 2000x10x2000 μm^3 and a prevailing internal pressure of 300 bar, low flowrates (of the order of 2 mm^3/min) are computed for liquids with viscosity 10^6 Poise. Such flowrates are low enough to exclude any damaging effects.

The calculation is conservative in the sense that the significant increase of viscosity as the molten glass is cooled when exiting the specimen through the crack, has been neglected.

FIGURE LEGENDS

Figure 1

Crystalline structure of boron nitride
♦ Boron o Nitrogen.

Figure 2

BIAXIAL CREEP MACHINE
T_{axial} = 100 KN, P_{int} = 40 MPa
temperature up to 700° C.

Table of Components.

1. Specimen
2. Zirconia particles or molten oxides
3. Zirconia or molten oxides compression mechanism
4. Furnace
5. Loading plates (tension)
6. Compression bars
7. Equal displacement mechanism for plates (5).
8. Equal displacement mechanism for plates (6).
9. Fixed plate (tension)
10. Moving plate (compression).
11. Fixed basement plates
12. Fixed bars
13. Articulated bars with pulleys
14. Sliders
15. Fixed bars with pulleys
16. Tension transmitter
17. Pulleys
18. Dead-weight
19. Cylinder-Slider
20. Bearing Sliders
21. Bearing Sliders
22. Compression transmitting bars
23. Hydraulic actuator
24. Compression transmitting bars
25. Compression transmitting rods
26. Spacer
27. Machine basement
28. Vacuum chamber
29. Machine columns

Figure 3

Specimen/compression pistons configuration

1. Ceramic piston
2. Graphite sealing
3. Zirconia particles
4. Specimen

Claims

1. Method of transmitting time varying pressure, characterised by the use of zirconia (ZrO_2) microspheres with granulometry 5 - 500 μm in the temperature range from -50° to 1600°C, and by the use of a mixture of molten oxides in the temperature range from 300° to 1100°C.

2. The method of Claim 1, further comprising the step that the basic molar composition of the mixture of molten oxides takes the form $xB_2O_3 \cdot (1\text{-}x)SiO_2$, with $0.2 \leq x \leq 1$. Depending on the desired viscosity, the operational temperature and the reactivity of the mixture, its composition may be modified by adding suitable quantities of other oxides that belong to the following categories :

i) Formers :	GeO_2, Al_2O_3, P_2O_5, V_2O_5, As_2O_5, Sb_2O_5, Sb_2O_3, Ga_2O_3, ZrO_2, As_2O_3.
ii) Conditional Formers :	TiO_2, MoO_3, WO_3, Cr_2O_3, ZnO, PbO, FeO, Fe_2O_3, CdO, ThO_2, In_2O_3, Bi_2O_3, PbO_2, SnO_2, HgO, MnO, CoO, NiO, BeO, SnO, TeO_2, Nb_2O_5, Ta_2O_5, HfO_2, ReO_2, TeO_2, RuO_2, OsO_2, Rh_2O_3, Ir_2O_3, IrO_2, PdO, PtO_2.
iii) Modifiers :	Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, Sc_2O_3, Tl_2O, Tl_2O_3, CuO, Cu_2O, Ag_2O, Au_2O_3, R_2O_3 (R = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dh, Ho, Er, Tm, Hb, Lu), SeO_2, PaO_2, UO_3.

Small quantities of alkali or alkaline earth halide salts, and sulfide or sulfate salts can also be added depending on the desired range of temperatures.

3. The method of Claims 1 & 2, further characterised by the fact that the transmitted pressure and/or the operational temperature may remain constant with time.

4. The method of claim 1, further characterised by the use if zirconia microspheres as pressure transmitting medium prefentially in the case of steady or monotonically increasing pressure under steady or time dependent temperature.

5. The method of claim 1, further characterised by a preferential granulometry of 20-100 μm for the zirconia particles and further comprising the step of coating the particles with a solid lubricant, preferentially boron nitride or molybdenum bisulfide.

6. The method of claim 1, further comprising the step that the microspheres may consist of other ceramics exhibiting high mechanical strength and resist-

ance to corrosive oroxidising environments and high temperatures, such as silicon carbide (SiC or SiSiC), silicon nitride (Si_3N_4) of different types, alumina (Al_2O_3), silica (SiO_2) or mixtures of these ceramics.

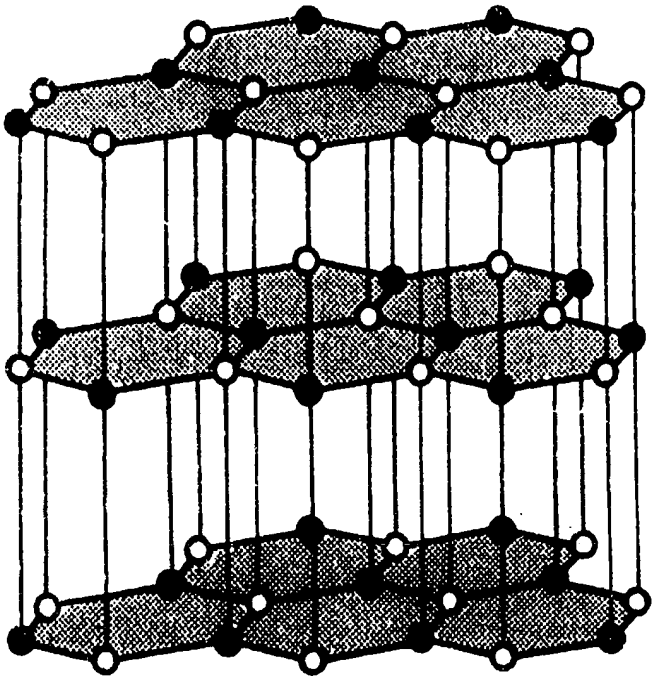

Figure 1

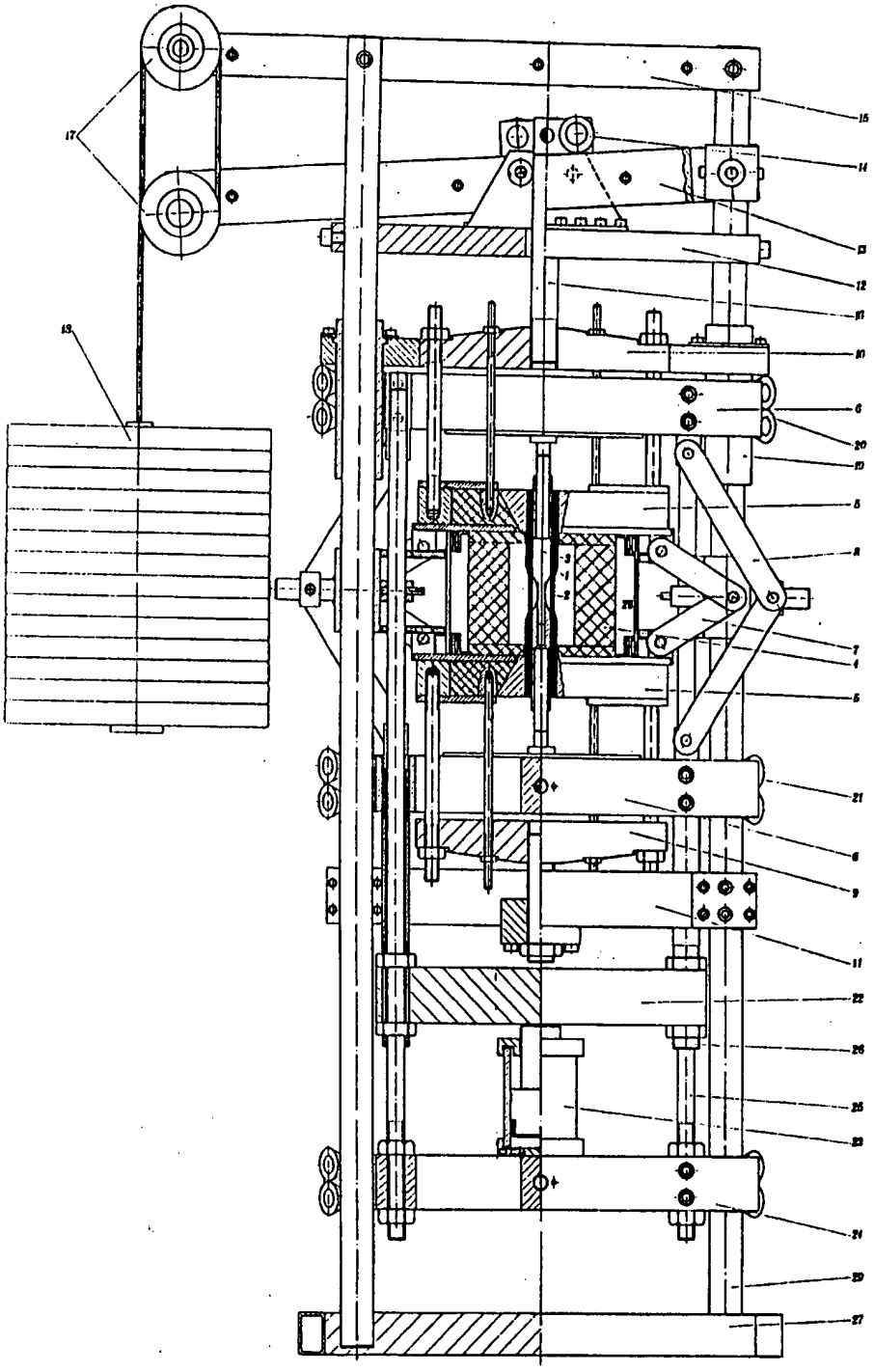

Figure 2

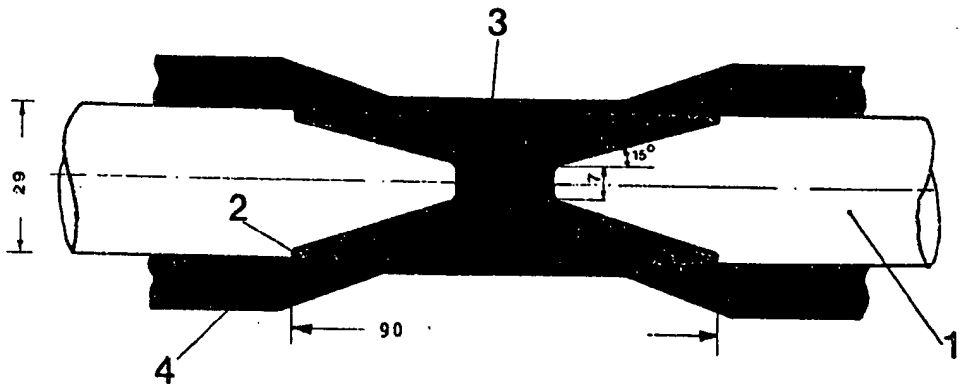

Figure 3

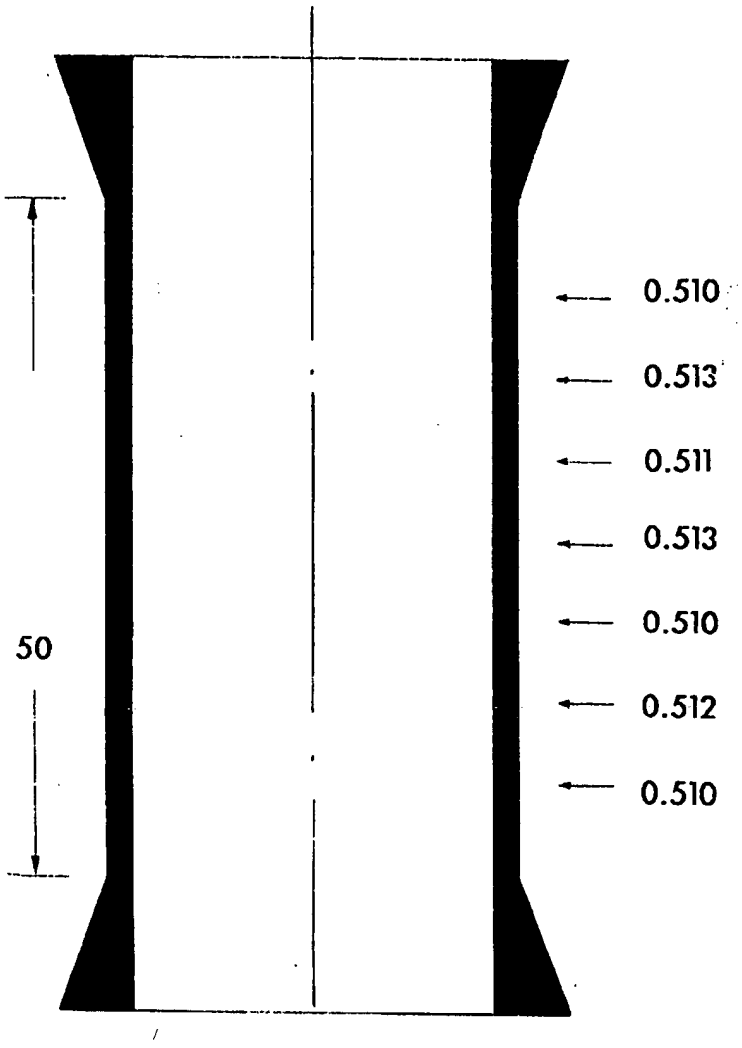

Figure 4

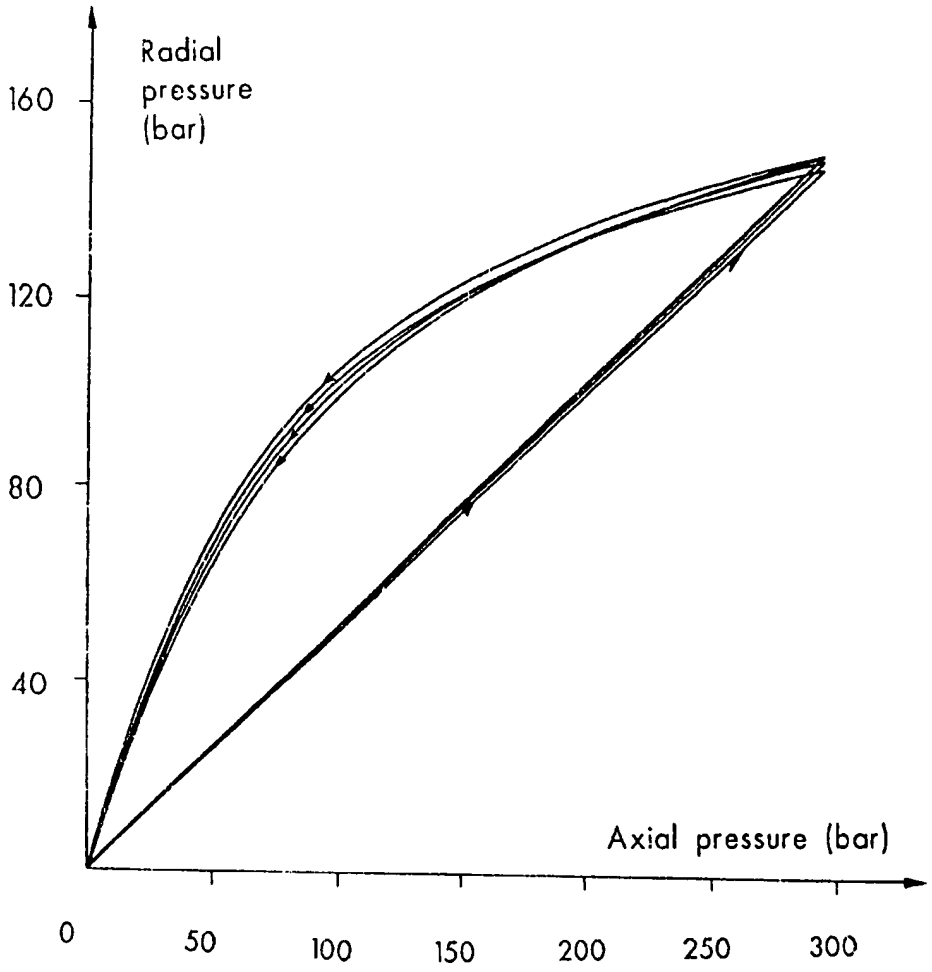
Radial
pressure
(bar)
160
120
80
40
Axial pressure (bar)
0
50
100
150
200
250
300

Figure 5

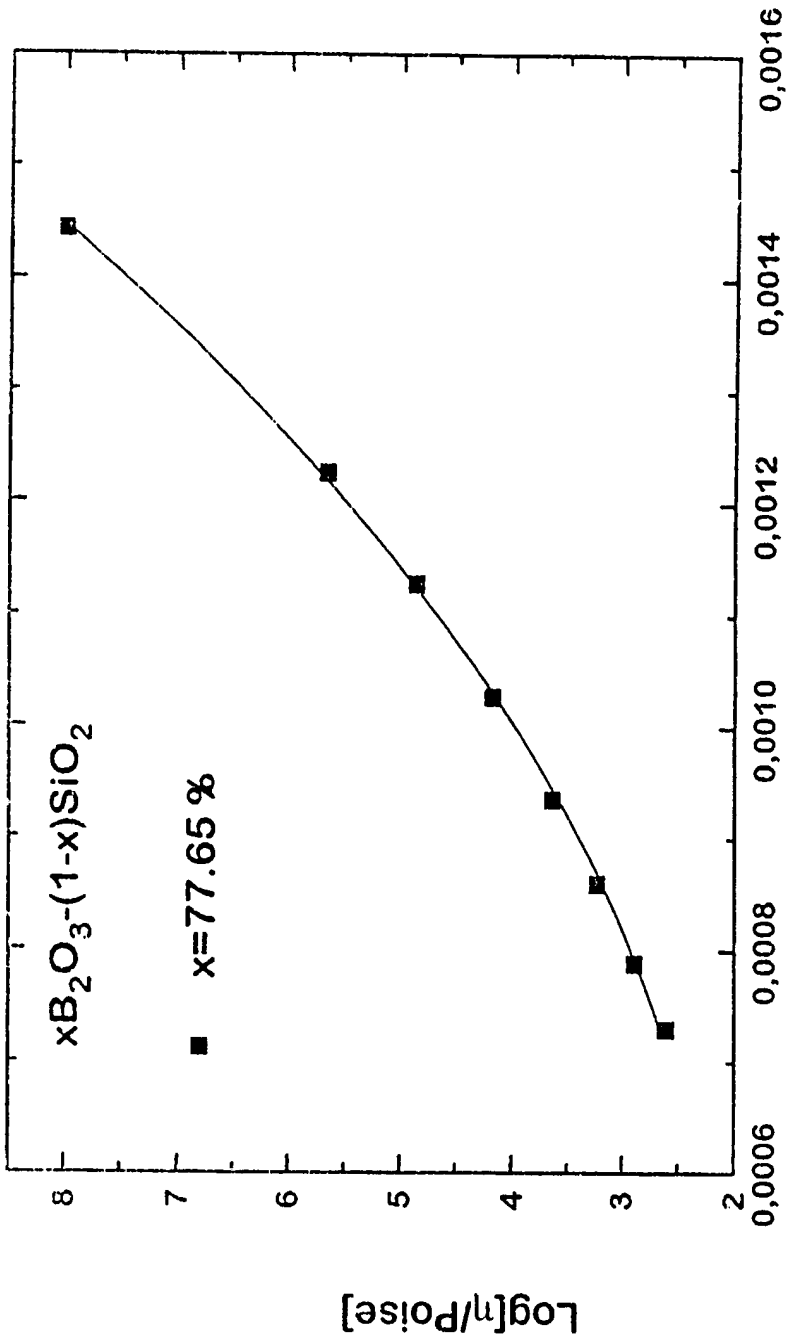
xB2O3-(1-x)SiO2
x=77.65 %
Log[η/Poise]
1/T (K-1)
8
7
6
5
4
3
2
0,0006
0,0008
0,0010
0,0012
0,0014
0,0016

Figure 6

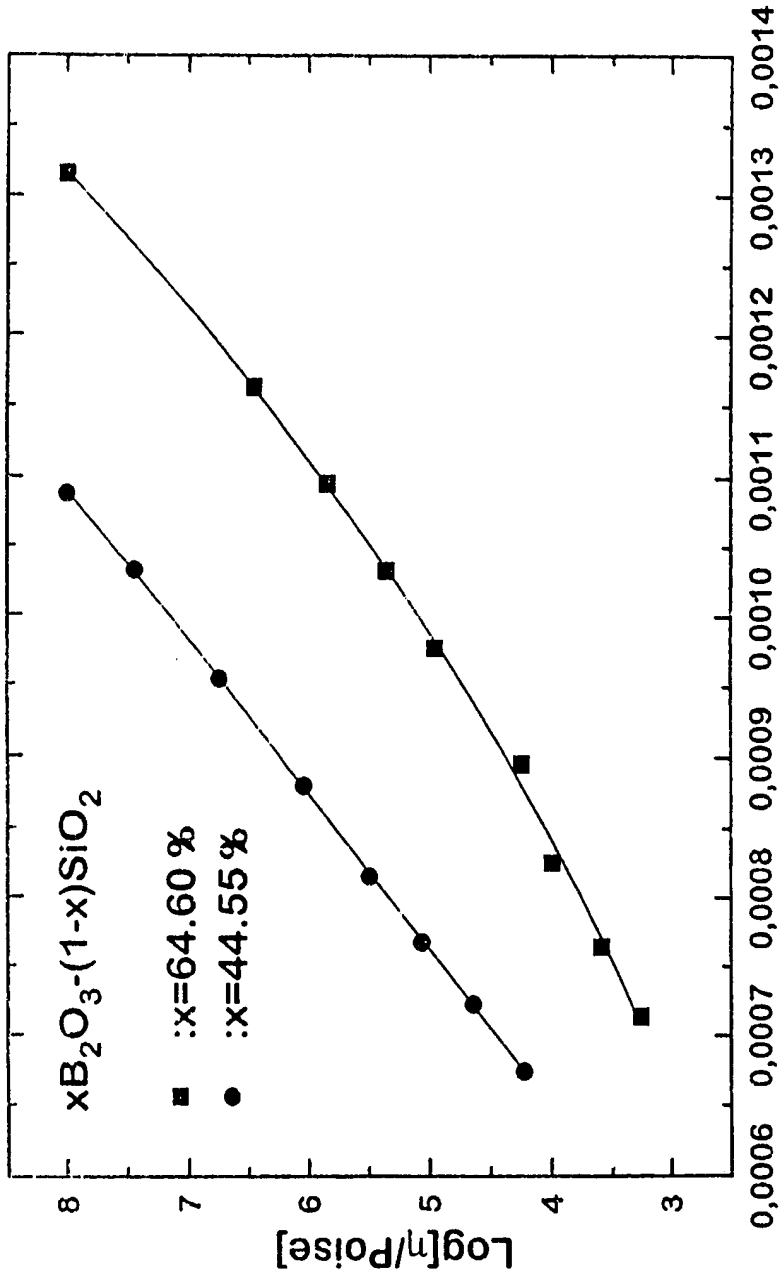
xB2O3-(1-x)SiO2
:x=64.60 %
:x=44.55 %
Log[η/Poise]
1/T (K-1)
8
7
6
5
4
3
0,0006
0,0007
0,0008
0,0009
0,0010
0,0011
0,0012
0,0013
0,0014

Figure 7

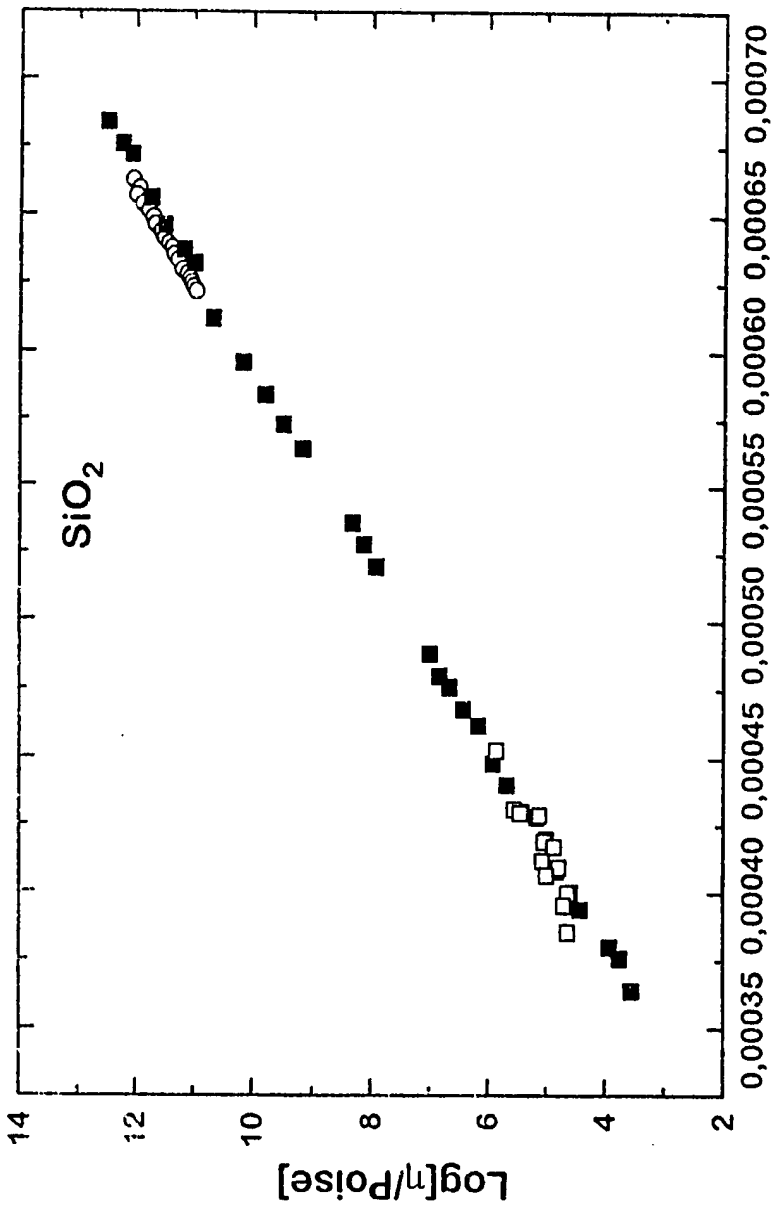
SiO2
Log[η/Poise]
1/T [K-1]
14
12
10
8
6
4
2
0,00035
0,00040
0,00045
0,00050
0,00055
0,00060
0,00065
0,00070

Figure 8

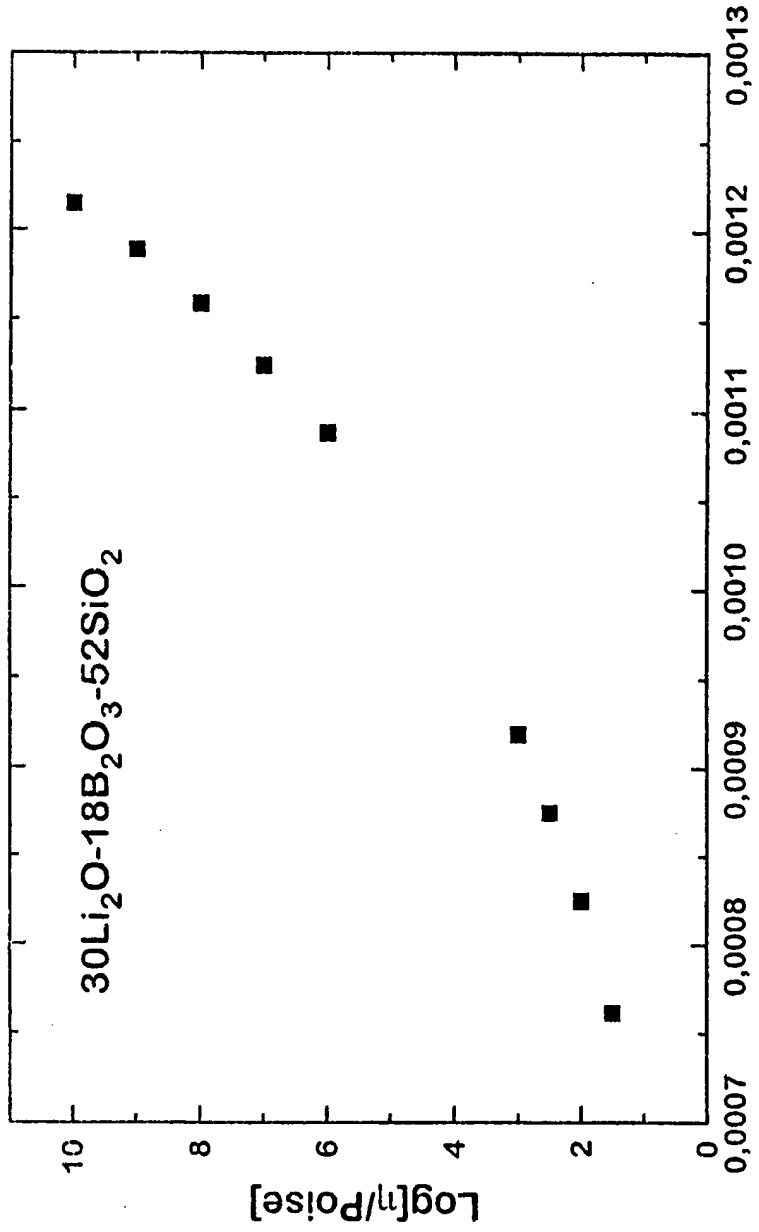
30Li2O-18B2O3-52SiO2
Log[η/Poise]
1/T [K-1]
10
8
6
4
2
0
0,0007
0,0008
0,0009
0,0010
0,0011
0,0012
0,0013

Figure 9

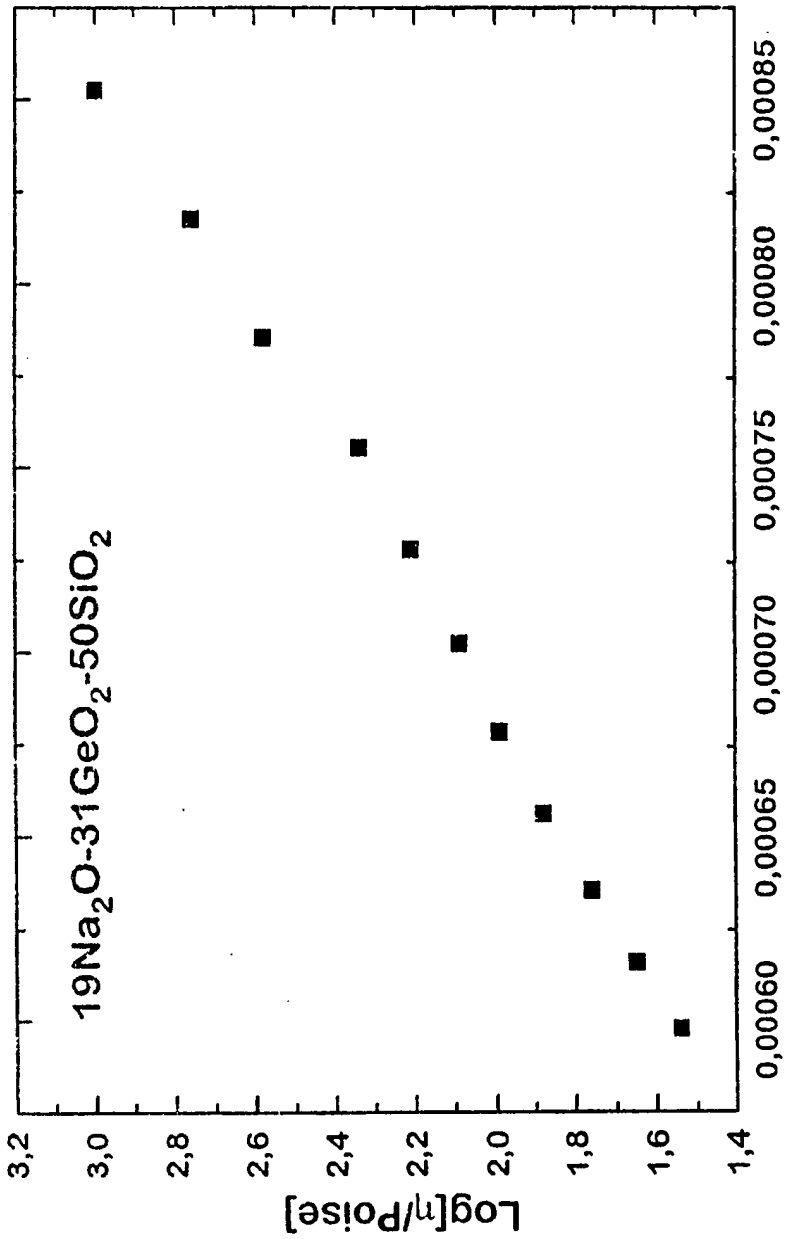
19Na2O-31GeO2-50SiO2
Log[η/Poise]
1/T [K-1]
3,2
3,0
2,8
2,6
2,4
2,2
2,0
1,8
1,6
1,4
0,00060
0,00065
0,00070
0,00075
0,00080
0,00085

Figure 10